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TiO_2 Nanotubes of Enhanced Nanocrystallinity and Well-Preserved Nanostructure by Pre-Annealing and Post-Hydrothermal Treatments

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Abstract. In the current investigation, a modified process combining pre-annealing and post-hydrothermal treatments has been applied on the as-dried TiO_2 nanotubes derived from alkaline route of TiO_2 P25 nanoparticles in 10 M NaOH solution. The combined treatment is purposely aimed at enhancing the nanocrystallinity of anatase TiO_2, while at the same time maintaining the integrity of the nanotube hollow structures. The detail of the structure, morphology and crystallinity of the resulting nanotubes were examined by XRD, SEM and TEM, while the optical properties of nanotubes were investigated by UV-visible spectroscopy. For the nanotube samples which have been previously annealed at 300°C, the crystallite size of anatase TiO_2 in nanotubes increased from 17.20 to 18.30 nm after being subjected to post-hydrothermal treatment at 100 to 150°C. The band gap energy (E_g) of the resulting nanotubes is inversely proportional to the crystallite size of anatase phase where the lowest value of 3.21 eV was obtained from the TiO_2 nanotube sample with the biggest crystallite size of 18.30 nm.

Keywords: TiO_2 nanotubes, amorphous, enhanced nanocrystallinity, post-hydrothermal
PACS: 61.46.Np, 61.43.Dq, 81.07.-b

INTRODUCTION

Inspired by the discovery of carbon nanotubes by Iijima in 1991 [1], one-dimensional TiO_2 nanotubes have attracted a great attention due to their novel properties and potential applications. In solar energy conversion, for example, one-dimensional (0-D) materials have shown several advantages because of their unidirectional electron transport properties [2]. By using nanotube with high aspect ratio, a facile electron transport from TiO_2 layer to the current collecting electrode can be achieved. The resulting "ballistic effect" prevents recombination of free electron with oxidized dye molecules, and thus leading to an expected higher light to electricity conversion efficiency. It has been observed that in water splitting, the use of TiO_2 nanowires to replace TiO_2 nanocrystalline films can enhance more than twice as in the photo-conversion efficiency [3]. Several other investigations also reported that TiO_2 nanotubes, in comparison to other forms of TiO_2, provide better properties in photocatalyst [4,5] and sensing devices [6]. Therefore, designing well-defined TiO_2 nanotubes is significant for fundamental investigation as well as various strategic applications.

Various methods of fabricating TiO_2-based nanotubes have been developed including assisted-template method [7], sol-gel process [8], electrochemical anodic oxidation [9], and hydrothermal treatment [10-12]. Hydrothermal treatment technique is considered as simpler, low-cost wet chemistry route and more suitable for scale-up in comparison to other methods. However, it is realized that the resulting crystalline nanostructures of nanotubes are still dominated by the sodium-titanate phase, instead of anatase TiO_2. Therefore, one of the challenges in this area is to find a suitable technique which can improve the crystallinity of anatase TiO_2 phase while at the same time maintaining the integrity of the nanotubes.

In our previous investigation, we proposed a modified technique combining a conventional pre-annealing process at 150°C for 6 hours, followed with post-hydrothermal treatments of different temperatures (80,100,120 and 150°C) for 24 hours. This technique has successfully converted the amorphous sodium-titanate phase to nanocrystalline anatase TiO_2, while preserving the tubular-shape integrity of nanotubes [13]. In the present work, we have increased the pre-annealing temperature up to 300°C, prior to similar

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post-hydrothermal treatments at 100, 120 and 150°C for 24 hours. This is to investigate whether a higher pre-annealing temperature could further increase the nanocrystallinity of anatase TiO_2 phase in nanotubes, without collapsing the tube structure itself.

EXPERIMENTAL DETAILS

To synthesize TiO_2 nanotubes, a certain amount of commercial anatase TiO_2 P25 powder (Degussa) was dispersed into ethanol solution of concentrated NaOH (10 M), followed with pre-hydrothermal treatment in a Teflon-lined autoclave. The autoclave was properly tightened and heated at 150°C for 48 hours in a drying oven. The obtained powder product was washed thoroughly with distilled water, further rinsed with 0.1 M HCl and finally washed again with distilled water until the pH value of the treated nanotubes became neutral, prior to drying to 110°C for 12 hours. The as-dried TiO_2 nanotubes were firstly subjected to conventional annealing process at various temperatures (300, 450 and 600°C) for 24 hours. For another group of samples, a different approached was carried out where the as-dried TiO_2 nanotubes was subjected to first conventional pre-annealing process at 300°C for 6 hours, followed with various post-hydrothermal treatments of different temperatures (100, 120 and 150°C) for 24 hours. The resulting TiO_2 nanotubes were characterized by using X-ray diffraction (Bruker AXS θ-2θ diffractometer using Cu K-α radiation of 1.5406 Å, operated at 40 kV, 40 mA). The crystallite sizes of TiO_2 nanocrystallite in nanotubes were estimated by using Scherrer's equation [14], while the estimated band gap energy (E_g) of TiO_2 nanocrystallites were obtained by analyzing the Kubelka Munk function [15] on the measured diffuse reflectance spectra using UV-1601, Shimadzu spectrophotometer at the wavelength range of 800−200 nm. Further confirmation on nanotube structures was carried out by performing observation using scanning electron microscopy/SEM (Leica Oxford Instrument, LEO 420i) and transmission electron microscopy/TEM (JEOL, JEM-1400).

RESULTS AND DISCUSSION

Figure 1 shows the XRD diffractogram of as-dried TiO_2 nanotubes and those subjected to the conventional annealing at 300, 450 and 600°C for 24 hours. The crystalline structure of as-dried sample is dominated by sodium titanate, $Na_xH_{2-x}Ti_2O_4(OH)_2$ (Θ). This formed is formed upon the ion exchange between Na^+ and H^+ during rinsing process with HCl. This ion exchange results in variation of surface tension which further causes the peeling of the titanate layers and thus wraps to form the nanotube structures [16]. By applying annealing process at 300°C for 24 hours, the diffraction peaks of the anatase (▲) and rutile (■) phases appeared as expected (Figure 1b), accompanied with the vanishing of several sodium titanates peak. Increasing annealing temperature to 450°C resulted in a higher intensity of anatase (101) and (200) peaks at 2θ of 25.30 and 48°, and further redution in the diffraction peaks of remaining sodium titatane (Figure 1c). With annealing at 600°C, finally, all the sodium titanate peaks have completely dissapeared and the sample became purely the mixture of anatase and rutile (Figure 1d).

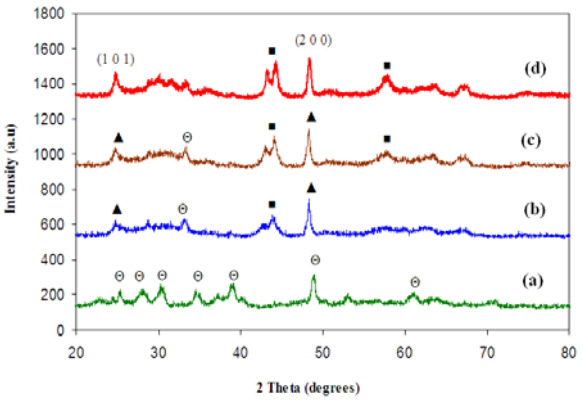

FIGURE 1. X-ray diffractogram of TiO_2 nanotubes after: (a) hydrothermal process and dried at 110°C for 12 hours; and conventional annealing for 24 hours at (b) 300,(c) 450, (d) 600°C.

Figure 2 shows the results of SEM observation on the as-dried TiO_2 nanotubes and nanotubes after being subjected to conventional annealing process at 300, 450 and 600°C for 24 hours. Apparently, the as-dried appeared as fibrous structures (Figure 2a). When the conventional annealing at 300-450°C was applied on the nanotube samples, however, the tubular shape has been deteriorated (Figures 2b and 2c), although in several locations such nanotube structure with shorter length still could be obtained. The nanotube structure was completely collapse and turned into granular form when the annealing temperature was further increased to 600°C (Figure 2d). The anatase crystallite sizes, as estimated by Scherrer's formula, for the as-dried nanotube and those annealed at 300, 450 and 600°C are 5.06, 9.79, 12.46, and 29.41 nm, respectively. These XRD and SEM studies showed that the conventional annealing up to 600°C provided an enhanced nanocrystallinity for anatase TiO_2 phase, but the integrity of nanotube structure cannot be properly maintained.

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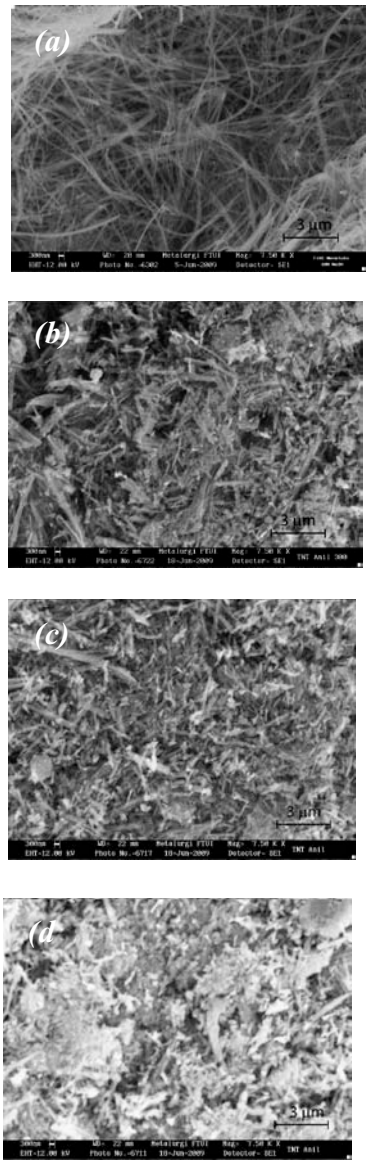

FIGURE 2. SEM images of: (a) as-dried nanotubes and after conventional annealing at (b) 300, (c) 450, and (d) 600°C.

Figures 3a-c shows XRD patterns for TiO_2 nanotubes that have been subjected to pre-annealing at 300°C, followed with post-hydrothermal treatment at 100, 120 and 150°C, respectively. It can be seen that as the post-hydrothermal temperature increased from 100 to 150°C, the intensity of sodium titanate diffraction peaks (♦) decreased, while on the other hand this is accompanied with an increase in diffraction peak intensity at 2θ of 25.30, 38.60 and 48.00, which belong to (101), (112) and (200) crystal planes of anatase TiO_2 phase (●). In order to confirm the formation of nanocrystalline anatase phase on those post-hydrothermally treated nanotubes, the diffraction peaks of TiO_2 P25 Degussa was also included for comparison (Figure 3d). As revealed by XRD analysis, the anatase crystallite size, as estimated by Scherrer's formula, for the post-hydrothermally treated TiO_2 nanotubes at 100°C, 120°C and 150°C are 17.20, 18.03 and 18.30 nm, respectively. In comparison to the crystallite size of anatase TiO_2 in our previous procedure with a pre-annealing temperature of 150°C which could only reach an average size of 7.81 nm [13], it is worth to note that by applying a higher pre-annealing temperature up to 300°C (with the same post-hydrothermal treatment) the resulting nanotubes in the current work can provide a much more pronounced crystallite size up to 18.30 nm.

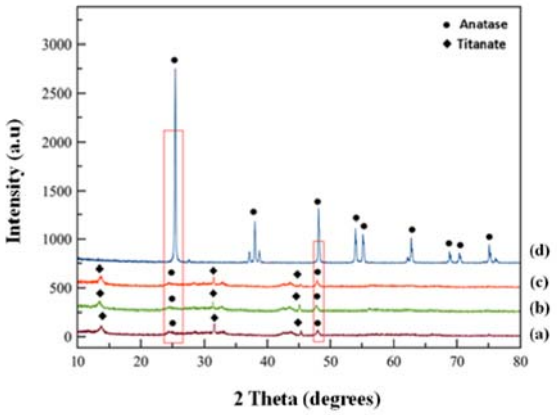

FIGURE 3. X-ray diffractogram of: TiO_2 nanotubes after post-hydrothermal treatment at: (a) 100°C, (b) 120°C, (c) 150°C; and (d) TiO_2 P25.

TEM images of the as-dried nanotubes are given in Figure 4a, while that of post-hydrothermally treated sample at 150°C are presented in Figure 4b. Figure 4a verifies that the resulting as-dried TiO_2 tubular structures, as observed by SEM in Figure 2a, are in fact the nanotubes. Referring to previous XRD study in Figure 1a it has been revealed that the as-dried nanotubes are not anatase TiO_2 yet but sodium titanate. The nanocrystallinity enhancement of the nanotubes resulted from post-hydrothermal treatment is demonstrated with the appearance of the dark areas in the tubular structures in Figure 4b. We expected that TEM images of these dark areas are the anatase TiO_2 phase growing along the wall of nanotubes. Selected area diffraction (SAD) on this post-hydrothermally treated nanotube has been performed to confirm the formation of nanocrystalline anatase TiO_2 (inset). The anatase TiO_2 grew as a compact and solid phase in the inner wall of nanotubes. This is rather different with our previous post-hydrothermal nanotubes at 150°C

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showing the disperse growth of TiO_2 phase on the outer wall of nanotubes.

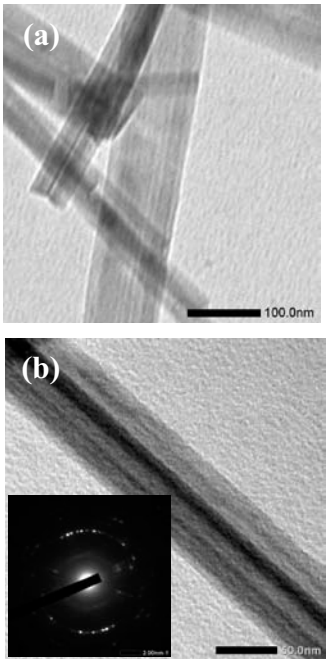

FIGURE 4. TEM images of: (a) as-dried sodium titanate nanotube; and (b) post-hydrothermally treated TiO_2 nanotube at 150°C.

The effect of nanocrystallinity on the electronic properties of post-hydrothermally treated TiO_2 nanotubes was investigated by UV-Vis spectroscopy. The resulting band gap energy (E_g) of TiO_2 nanocrytallites estimated by using Kubelka Munk function provided the value of 3.39, 3.23 and 3.21 eV for TiO_2 nanotubes which have been subjected to post-hydrothermal treatment at 100, 120 and 150°C, respectively. As the post-hydrothermal treatment temperature was increased from 100°C to 150°C, the band gap energy of TiO_2 nanotubes was reduced by 5.6%. This is related to the growth of TiO_2 nanocrystallite as has been studied by previous XRD and TEM. This confirms that in nanometer regime, the crystallite size of semiconductor nanostructures such as TiO_2 significantly affects the band gap energy. The smallest band gap energy in the present work (3.21 eV) is very close to that of bulk anatase TiO_2, which is 3.20 eV. This is beneficial for the application of this nanotube for dye sensitize solar cell (DSSC) since it can facilitate the electron excitation from valence band to conduction band by photon energy in the visible range.

CONCLUSION

A modified process combining pre-annealing treatment at 300°C for 6 hours and post-hydrothermal treatment at 100°C-150°C has been successfully devised to enhance the nanocrystallinity of anatase TiO_2 phase in nanotubes significantly while maintaining the integrity of tubular nanostructures. The well-preserved nanotube after a sequence process of pre-annealing at 300°C and post-hydrothermal treatment at 150°C provided the biggest crystallite size of 18.30 nm and the lowest value band gap energy (E_g) of 3.21 eV.

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